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THE EFFECTS OF SULFIDES ON ANAEROBIC TREATMENT

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by

Alonzo Wm. Lawrence, Perry L. McCarty, and
Fernand J. A. Guerin

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Anaerobic waste treatment is a biological process. As such it depends for successful operation on the maintenance of a proper environment for the organisms involved. By delineating this proper environment, a more complete understanding of the process will be attained. This will lead to an increase in the operational control and predictability of anaerobic treatment. Temperature, pH, nutrient requirements, and materials producing toxic effects are among the important environmental parameters. Special attention must be focused on the problem of toxicity-causing substances if anaerobic treatment, long a mainstay of municipal sewage treatment, is to be successfully extended to the treatment of complex industrial wastes. Many of these wastes are certain to contain a greater variety and higher concentration of inorganic salts than would be expected in municipal wastes. Recent studies[1][2] have reported the effects of several cations on the methane fermentation. Sulfide is an anion which occurs in many wastes, or can be produced by biological action on the wastes, and it may be a limiting factor in the anaerobic treatment of many industrial wastes. The effects of high sulfide concentrations on anaerobic treatment are not well understood, and were explored in this investigation.

Previous Studies

Reports on the role of sulfides in anaerobic treatment have appeared in the literature at various times. Rudolfs and Zeller[3] reported the effects of several sulfate salts on the digestion of seeded, fresh solids. Sulfate reduction to sulfide was indicated. A decrease in gas production and volatile matter reduction occurred, the extent varying from salt to salt. In general, gas production was retarded more severely than volatile matter reduction.

In connection with the treatment of white water wastes, Rudolfs and Amberg[4][5] investigated the effects of soluble sulfides on the digestion of both seeded white water and sewage sludge. In the case of sewage sludge, the addition of 200 mg/l of sulfides decreased gas production by 70 percent, and volatile matter reduction by 50 percent. From a slug feed study of acetate fermentation, it was concluded that methane fermentation was a linear function of soluble sulfide concentration, and that no methane was formed with sulfide additions above 165 mg/l as sulfur. However, additions up to 300 mg/l of soluble sulfides were felt to have little effect on the production of volatile acids. These investigators studied several methods for controlling the soluble sulfide concentration in laboratory digesters receiving white water concentrate. It was concluded that stripping of the sulfides by intermittent passage of inert gas through the digesting mixture was the most advantageous of the methods tested.

Aulenbach and Heukelekian[6] studied the effects of sulfides on digestion of seeded fresh solids at 20°C. The addition of 100 mg/l sulfides fed as Na_2S retarded gas production by 50 percent compared to a control. The solubility and concentration of the sulfide salts used were considered important in determining the effects of sulfides on digestion. Also, the methane organisms were felt to be most severely affected by high sulfide concentrations.

None of the above studies were conducted with digesters in equilibrium daily operation. Therefore, neither the ability of the microorganisms to adapt to higher sulfide concentrations, nor the effect of loss of gaseous sulfide on the permissible concentration in the waste could be evaluated. Hence, the need for additional studies is indicated, so the role of sulfides in modern digester operation with daily feed and mixing can be better understood.

Theoretical Considerations

An evaluation of the possible effects of sulfides on anaerobic treatment must consider (1) the total quantity of sulfides either entering the digester or produced during treatment, and (2) how these sulfides are distributed within the digester. These two factors are discussed in the following.

Quantity of Sulfides

Sulfides in anaerobic treatment can result from (1) introduction of the sulfides with the raw waste and/or (2) biological production in the digester from reduction of sulfates and other sulfur-containing inorganic compounds, as well as from anaerobic protein degradation. Sulfate salts would probably be the major precursors of sulfides in most industrial wastes. Biological reduction of sulfates to sulfides has been studied extensively[7][8]. The digester environment fulfills the conditions necessary for sulfate reduction, namely, low ORP, presence of degradable organic matter, proper temperature, and sulfates, as described by Heukelekian[9].

The principal organism involved in sulfate reduction is believed to be Desulfovibrio desulfuricans. This organism is a strict anaerobe. It derives energy for synthesis and maintenance from the metabolism of organic matter, and uses sulfate as its terminal electron acceptor. The reduction of sulfates in this process may be expressed by the following equation:

$$8H^+ + 8e^- + SO_4^= \xrightarrow[\text{bacteria}]{\text{sulfate-reducing}} S^= + 4H_2O \qquad (1)$$

The reduction of one mole of sulfur (32 grams) by this process corresponds to the oxidation of 8 equivalents of organic matter, or approximately 64 grams on a COD or oxygen-equivalent basis.

Another way in which sulfides are formed in anaerobic treatment is from the degradation of sulfur-containing amino acids in proteins. This was shown by Aulenbach and Heukelekian[6] in their studies on the anaerobic degradation of the sulfur-containing amino acids, cystine and methionine.

Thus, a proper evaluation of the potential effects of sulfides on anaerobic waste treatment must consider all possible sulfide precursors in the raw waste. As indicated above, this includes the sulfides entering with the waste, the sulfides resulting from inorganic sulfur reduction, and the sulfides resulting from protein decomposition.

Distribution of Sulfides

Sulfides in the digester may be present in a soluble or insoluble form, depending upon the cations with which they are associated. Several of the common metal sulfides such as iron, copper, zinc and nickel are insoluble, and thus heavy metal cations quantitatively precipitate and remove the sulfides from solution. The remaining soluble sulfide forms a weak acid which ionizes in aqueous solution, the extent depending upon the pH. Thus, it is possible to have H_2S, HS^-, and $S^=$ in solution. At the neutral pH required for anaerobic treatment, only the first dissociation of hydrogen sulfide is of importance, as follows:

$$H_2S_{aq} \rightleftarrows H^+ + HS^- \qquad (2)$$

The mass action equation for this equilibrium is:

$$\frac{[H^+]\,[HS^-]}{[H_2S_{aq}]} = K_1 \qquad (3)$$

Because of the limited solubility of hydrogen sulfide, a certain portion of that formed will escape with the digester gas produced. The resulting equilibrium between hydrogen sulfide remaining in the digester supernatant liquor and that in the gas above is governed by Henry's Law as follows:

$$[H_2S_{aq}] = \alpha [H_2S_g] \qquad (4)$$

Here, $[H_2S_{aq}]$ and $[H_2S_g]$ are expressed in units of moles per liter of liquid, and moles per liter of gas, respectively. Values for the equilibrium constant, K_1, and the absorption coefficient, α, for sulfides are shown in Table 1 for various temperatures. The values for α were taken from the Handbook of Chemistry and Physics[10], while the values for K_1 were computed for various temperatures using both the van't Hoff equation and data from this reference.

TABLE 1

VALUES FOR SULFIDE EQUILIBRIUM CONSTANTS[10]

Temperature °C	Ionization Constant K_1	Absorption Coefficient α
18	9.1×10^{-8}	2.72
25	11.2×10^{-8}	2.28
35	14.9×10^{-8}	1.83
45	19.4×10^{-8}	1.52

A consideration of the relationship between pH and the different forms of soluble sulfide, as well as the solubility of hydrogen sulfide gas itself, allows prediction of the distribution of the sulfides between the gas and aqueous phases as follows, where the total concentration of soluble sulfides is expressed as [T.S.S.]:

$$[T.S.S.] = [HS^-] + [H_2S_{aq}] \tag{5}$$

Substituting for $[HS^-]$ from Equation 3 yields:

$$[T.S.S.] = \frac{K_1 [H_2S_{aq}]}{[H^+]} + [H_2S_{aq}] \tag{6}$$

Substituting for $[H_2S_{aq}]$ from Equation 4 then yields:

$$\frac{[T.S.S.]}{[H_2S_g]} = \alpha \left(1 + \frac{K_1}{[H^+]}\right) \tag{7}$$

From the above equation, it is possible to calculate the equilibrium ratio for the concentration of soluble sulfides in the digester supernatant liquor to the concentration of hydrogen sulfide in the gas, knowing only the digester pH and temperature. These equations could be modified to include the effect of ionic strength on the activities of the various ions, however, this modification did not appear to be justified because of other more significant variables which would prevent a complete equilibrium between the gas and liquid phases from taking place in a digester.

Experimental Procedure

The experimental portion of this study was conducted (1) to determine the effect of various concentrations of soluble sulfide on anaerobic treatment, (2) to determine the effect of insoluble sulfides on anaerobic treatment, and (3) to attempt to experimentally verify the soluble sulfide relationship developed above. It was desired to have the experimental conditions simulate modern full-scale digester operation as closely as possible. To achieve this, a series of 1.5-liter laboratory digesters connected as shown in Figure 1 were operated on a 20-day detention time at 35°C. The digesters were mounted on a shaking platform to obtain continual mixing of the digester contents. The gas produced was collected for measurement over an acidified salt solution and expelled daily. The digesters were fed with Menlo Park, California, primary settled raw sewage sludge diluted approximately 1:1 with tap water. A volume equal to the sludge addition volume of 75 ml was withdrawn daily for analysis. The average characteristics of the raw sludge feed during this study are shown in Table 2.

TABLE 2

RAW SLUDGE FEED CHARACTERISTICS

Total Solids	1.73 percent
Volatile Solids	80 percent of Total
COD	24,000 mg/l
Loading Rate	0.05 lbs. v.s./day/ft^3

To establish equilibrium operation, the digesters were operated for 60 days prior to the beginning of the sulfide addition. Daily introduction of sulfides was accomplished by combining 5 ml of sulfate solution with the daily raw sludge feed. These solutions were prepared from Na_2SO_4 for soluble sulfide studies, and from $FeSO_4$, acidified with HCl to prevent precipitation of air-oxidized iron, for insoluble sulfide studies. The use of sulfide precursors rather than sulfide-containing compounds simulated the expected major source of sulfides in field digesters, and also avoided the many problems inherent in the use of a solution of soluble sulfides.

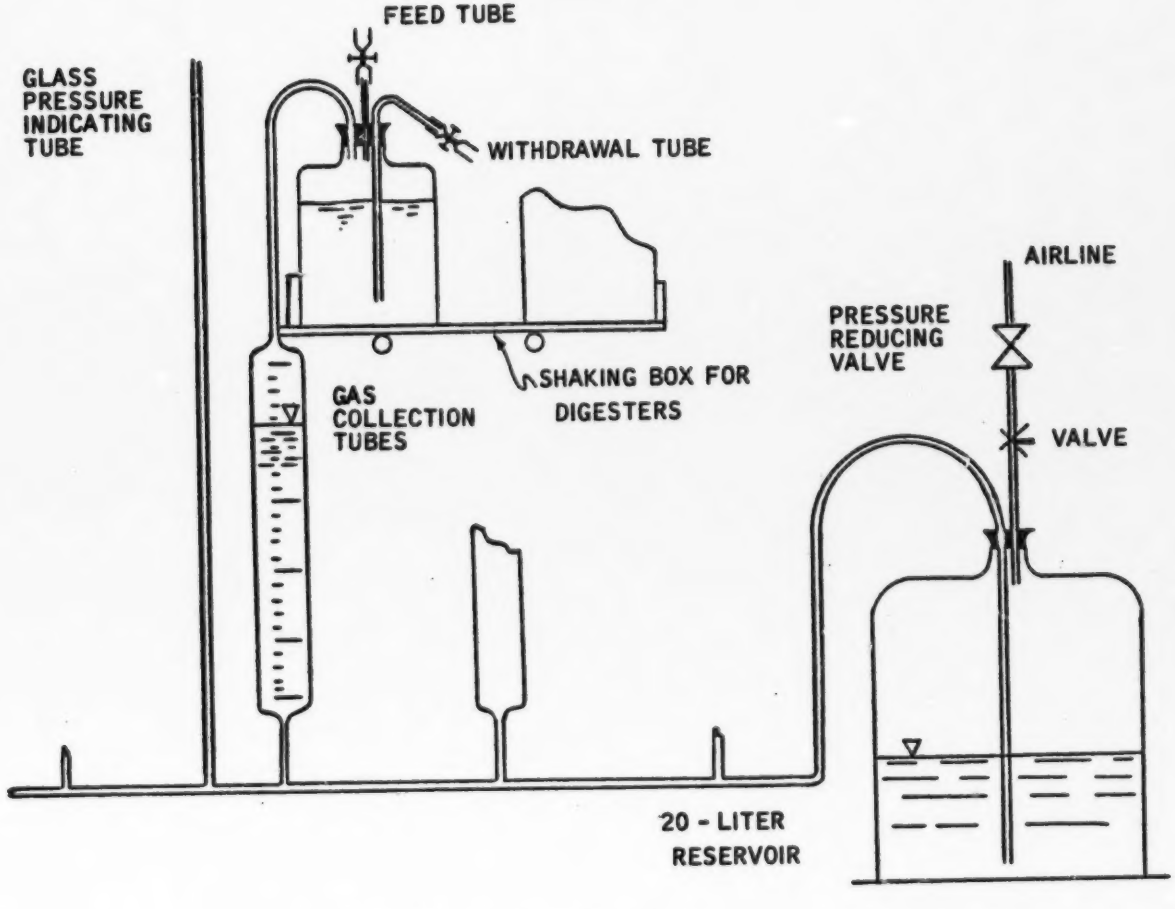


Figure 1 - Daily Feed Digester System

Four digesters were used in this study and the initial sulfur concentrations in the daily feed were: (1) Na_2SO_4, 200 mg/l as S; (2) Na_2SO_4, 400 mg/l as S; (3) $FeSO_4$, 400 mg/l as S; and (4) 0 mg/l S (control). After 85 days of operation, the sodium sulfate addition rate in the 400 mg/l S unit was increased to 800 mg/l as S for 62 days, and then to 1,200 mg/l as S. The sodium sulfate feed rate in the initial 200 mg/l S unit was increased to 1,600 mg/l as S after 57 days of operation. The $FeSO_4$ unit and the control were unchanged throughout the study. The aliquots of digester contents withdrawn daily were frequently subjected to routine analyses for process control. Analyses performed were pH, alkalinity, total volatile acids by extraction technique[11], total and volatile solids, and digester gas analysis by gas chromatography. Total and soluble sulfides were determined according to the titrametric method for sewage[12], using a 25-ml sample. For soluble sulfides, the samples were placed immediately after collection into centrifuge tubes containing 0.1 ml each of 6 N $AlCl_3$, and 6 N NaOH. The completely filled tubes were stoppered and centrifuged for five minutes at low speeds (4 to 5 x 10^3 rpm). A 25-ml volume of the centrifuged supernatant was subjected to the recovery technique employed for total sulfides. The sulfide recovery efficiency, exclusive of the centrifugation step, was found to be in the 92 to 100 percent range as determined from a series of known Na_2S solutions having sulfide concentrations as S of 0 to 1,100 mg/l. Sulfides in the digester waste gas were determined by expelling the collected gas through a zinc acetate solution, and then proceeding with the iodine-thiosulfate back titration. All sulfide values presented are as directly measured.

Experimental Results

The average daily gas productions for the control unit, and the units receiving 200 and 400 mg/l S in the form of sodium sulfate, are shown in Figure 2. For the 54-day period shown, the average daily gas production expressed as a percent of the control gas production was 96.2 percent for the 200 mg/l S unit, and 94.2 percent for the 400 mg/l S unit. Analysis of the gas produced by the control digester showed the percent of methane to vary between 65.1 and 67.8 percent, and that of CO_2, between 34.9 and 32.2 percent. Gas analysis on the 200 and 400 mg/l S units indicated they contained about 2 to 3 percent higher methane than the control, due to the increased retention of CO_2 in solution as bicarbonate, as explained later. Volatile acid concentrations for these units were comparable to those in the control, the maximum being only 72 mg/l as acetic acid.

The expectation that the added sulfates would be reduced rapidly by biological action was borne out by the sulfide analyses performed on the digester supernatant liquor and gas samples. Concentrations of total and soluble sulfides in solution, as well as sulfides in the gas, (all as sulfur) for the 400 mg/l S unit and the control are shown in Figure 3. A comparison between the sulfide concentrations for these two units indicates that the additional sulfides formed from sulfate reduction were present in the soluble form. A similar relationship between the sulfides formed was attained in the 200 mg/l S unit. Equilibrium soluble sulfide concentrations were 32 mg/l S, and 78 mg/l S, in the 200 and 400 mg/l units, respectively.

Figure 4 shows the average daily gas production and sulfide concentrations in the units receiving 800, 1200 and 1600 mg/l S, respectively. Average daily gas production for the 800 mg/l S was 88.9 percent of the control gas production over the period studied. The soluble sulfide concentration increased from about 170 mg/l at day 10 to about 200 mg/l during the last 20 days at this sulfur feed concentration. However, at no time in the 62 days of operation did the volatile acid concentration in this unit rise above 58 mg/l as acetic acid. As with the 200 and 400 mg/l units, gas analysis revealed methane percentages slightly above those of the control.

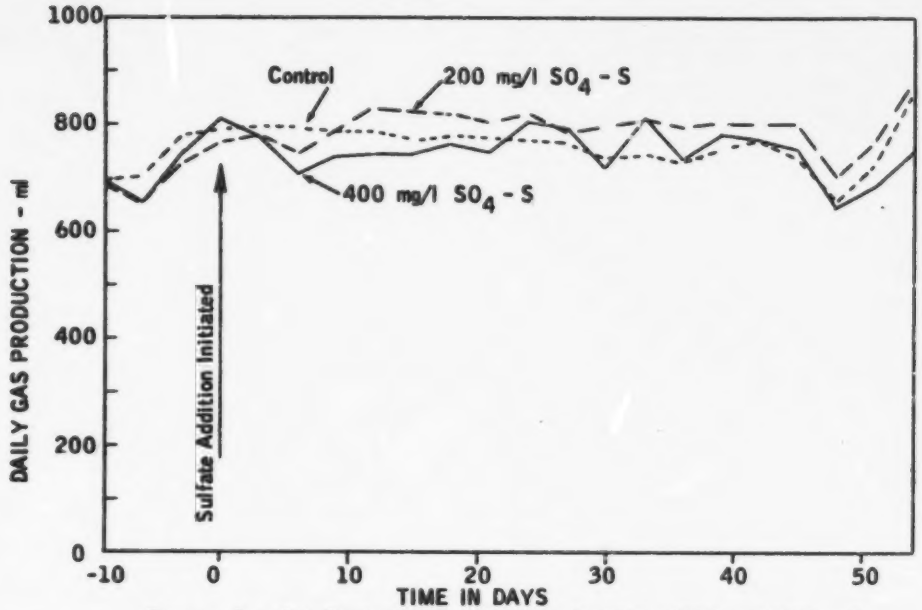


Figure 2 - Gas Production for Digesters Receiving 200 and 400 mg/l Sulfate Sulfur and Control

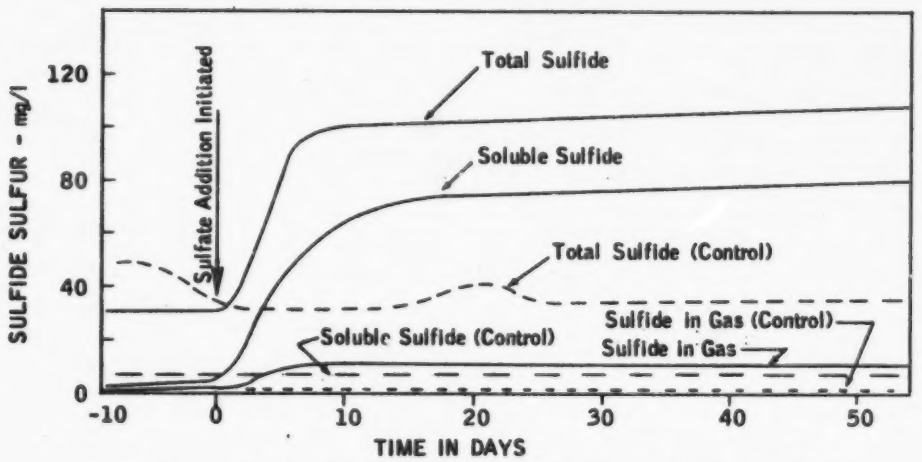
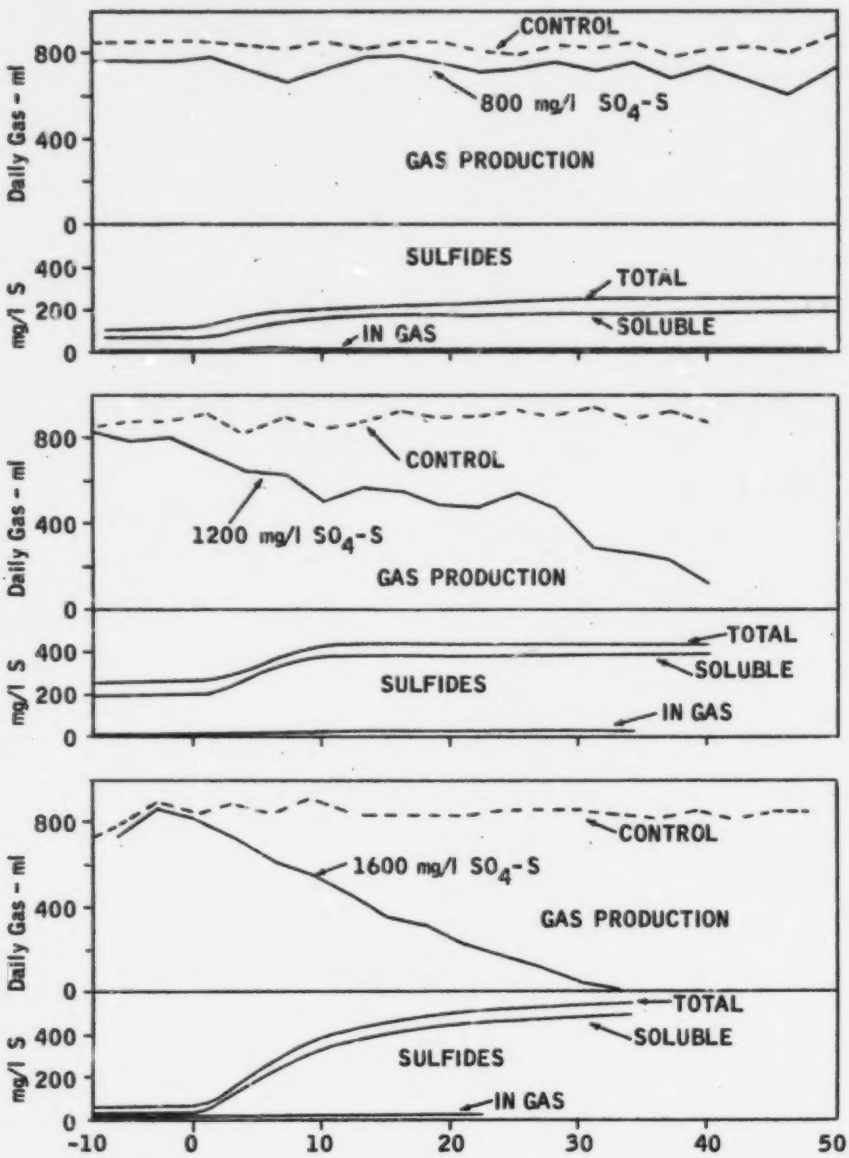


Figure 3 - Sulfide Concentrations for Digester Receiving 400 mg/l Sulfate Sulfur and Control



TIME IN DAYS AT INDICATED SULFATE CONCENTRATION

Figure 4 - Daily Gas Production and Concentration of Sulfides for Digesters Receiving 800, 1200, and 1600 mg/l Sulfate Sulfur

When the sulfur concentration in the 800 mg/l S digester feed was increased to 1,200 mg/l S, toxic conditions resulted. Gas production ceased within 40 days. The soluble sulfide concentration rose to 300 mg/l S by the fifth day and to 390 mg/l S by the 34th day. The volatile acids concentration and gas production for this unit are shown in Figure 5. The gas production had decreased to approximately 50 percent of that of the control before a significant increase in volatile acid concentration occurred. On day 33, when gas production had dropped to 27 percent of the control. the percent of methane in the gas was still 64.2 percent.

As shown in Figure 4, toxic conditions also resulted when the sulfide concentration in the 200 mg/l S unit was increased to 1,600 mg/l. Measured soluble sulfide concentrations reached 402 mg/l S by the 12th day, and attained a final value of 495 mg/l S by the end of the run. The volatile acids concentration and gas production for this unit are also shown in Figure 5. Again, it can be seen that gas production declined to approximately 50 percent of the control before a significant increase in volatile acids resulted. On day 21 when gas production had fallen to 20 percent of the control, the gas contained 70.3 percent methane. Thus, it appears sulfides initially affect the acid-producing organisms as much or more than the methane formers. This also indicates that an increase in volatile acids would not be a reliable indicator for the onset of sulfide toxicity. Soluble sulfide analysis is probably the best control.

The pH and alkalinity of the digester mixed liquor at the termination of each phase of the study, along with predicted increases in alkalinity due to reduction of sulfate (strong acid) to sulfides (weak acids) are shown in Table 3. The close agreement between predicted and measured alkalinities is a further indication that total reduction of sulfates to sulfides was accomplished throughout these studies.

TABLE 3

pH, INCREASE IN, AND TOTAL ALKALINITY OF DIGESTERS

Feed SO_4- S mg/l	pH	Calculated Alkalinity -mg/l Increase	Total	Measured Alkalinity - mg/l
(0) Control	7.0	0	----	1650
200	7.1	620	2270	2100
400	7.1	1250	2900	2900
800	7.3	2500	4150	4400
1200	6.9	3750	5400	5100
1600	7.2	3333	4983	4900

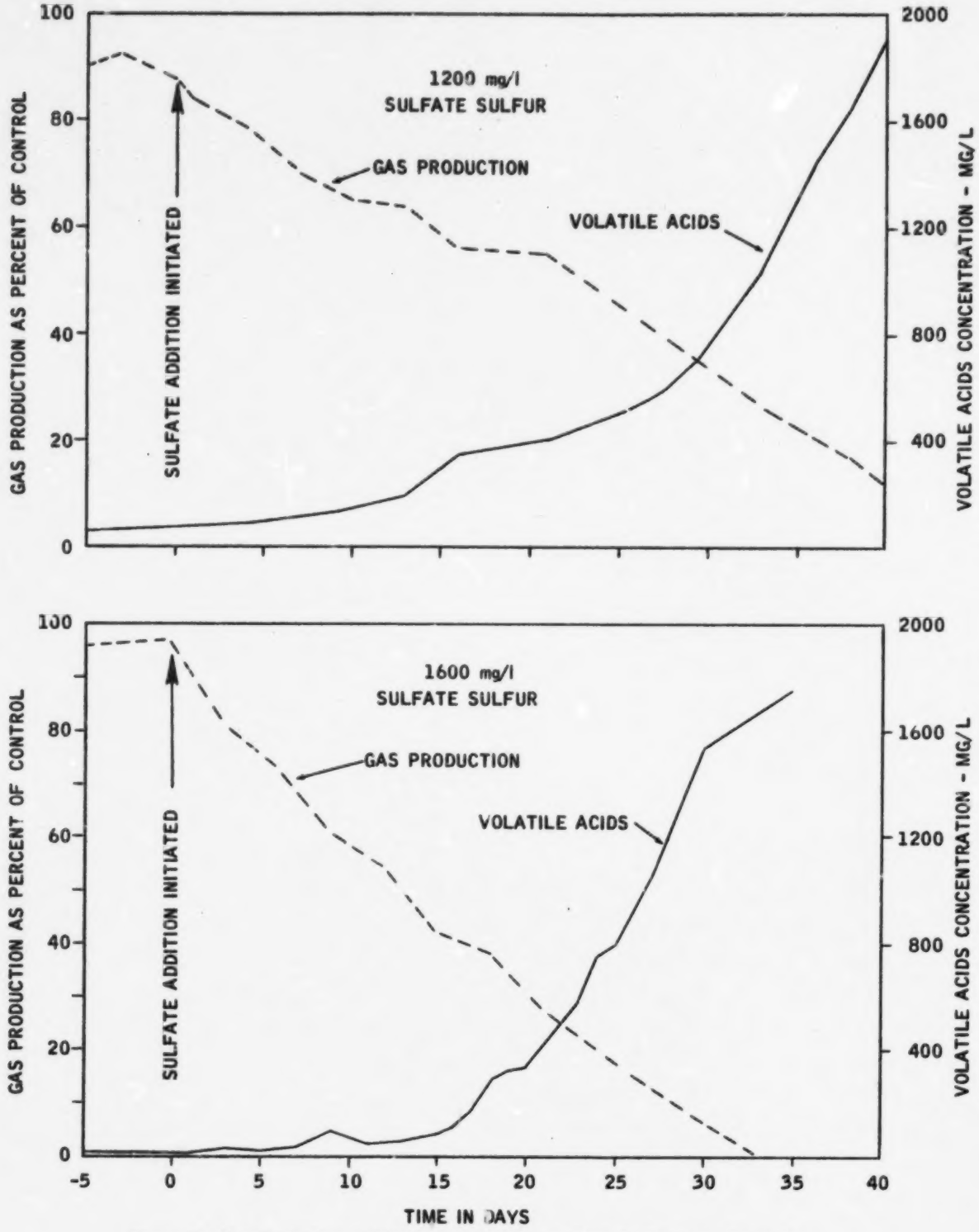


Figure 5 - Gas Production and Volatile Acids Versus Time for Digesters Receiving 1200 mg/l and 1600 mg/l Sulfate Sulfur

Average daily gas production and sulfide concentrations for the digester fed 400 mg/l $FeSO_4$ as S are shown in Figures 6 and 7. The average daily gas production over the study period was 91.0 percent of the control for the same period. Volatile acid concentrations were comparable to those in the control, with the maximum being 50 mg/l as acetic acid. Here, the unit with iron to precipitate the sulfides when formed operated very well, even with total sulfide concentration as high as 400 mg/l. This indicates that only the soluble sulfides are inhibitory to anaerobic fermentation, and not the insoluble sulfides.

Discussion

Sulfide Toxicity

Soluble sulfides can produce toxic or inhibitory effects in anaerobic treatment as shown by the experimental results of this study. This toxicity is initially evidenced by a decrease in gas production and finally in severely retarded digestion, by an increase in volatile acids concentration. The decrease in gas production was not significant (less than 12 percent) in the digesters having equilibrium soluble sulfide concentrations up to 200 mg/l S. This latter concentration occurred in the digester receiving Na_2SO_4 at a concentration of 800 mg/l as S. In the two laboratory units containing greater than 200 mg/l soluble sulfide, the toxic effects resulted in total cessation of gas production and a significant volatile acid accumulation.

The results of this study indicate that the relationship between gas production as a percent of the control and soluble sulfide concentration is not linear. The gas production decreased gradually with increasing sulfide concentration up to a "threshold" value, beyond which severe toxicity and total cessation of gas production resulted. From this study the "toxic threshold" for soluble sulfide appears to lie at about 200 mg/l. This type of toxic effect agrees with the rather broad zone of slightly sub-optimal operation noted by Kugelman and McCarty[2] for cation toxicity. It is at variance with the linear relationship derived from slug studies by Rudolfs and Amberg[4]. Such a discrepancy points out the difficulty, at

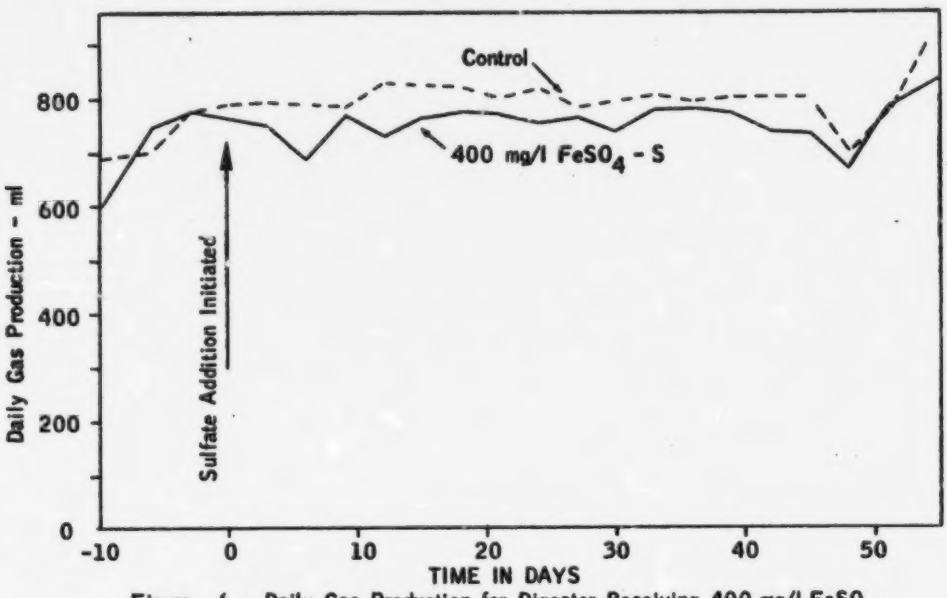


Figure 6 - Daily Gas Production for Digester Receiving 400 mg/l $FeSO_4$ Sulfur

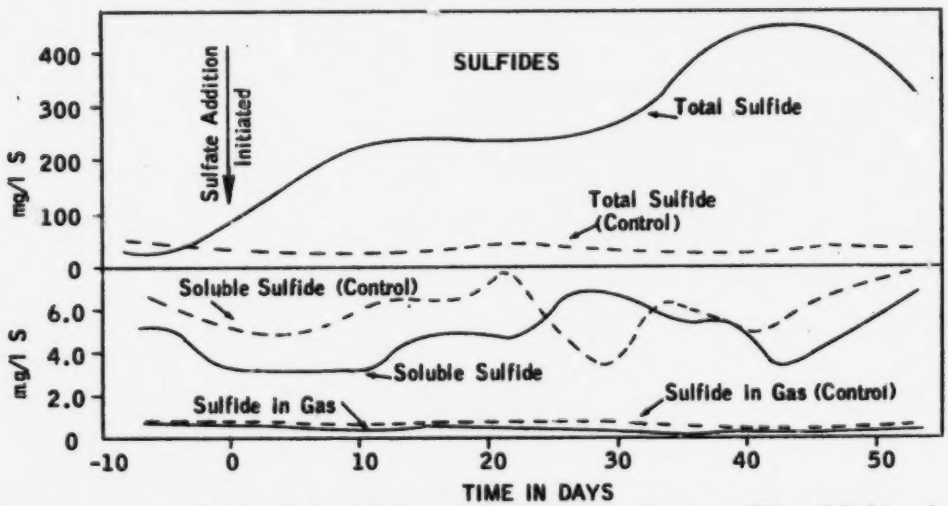


Figure 7 - Sulfide Concentrations for Digester Receiving 400 mg/l $FeSO_4$ -S and Control Digester

least with sulfides, in extrapolating results of uncontrolled slug studies to continuous operation. The daily addition of sulfides or sulfide precursors to digesters under conditions more closely approximating full-scale operations presents a different picture of the tolerance of anaerobic treatment to soluble sulfides.

Also, as indicated by others, insoluble sulfides appear to exert relatively minor effects on anaerobic treatment, as evidenced by the results obtained from the digester receiving $FeSO_4$. The iron sulfides formed would be insoluble as evidenced by the solubility product of the most probable form present, ferrous sulfide:

$$K_{sp} = 3.7 \times 10^{-19} \text{ at } 18^{\circ}C. \quad (10)$$

That this was the case is evident from the results of the sulfide analyses. These analyses showed that although the soluble sulfide concentration was lower than in the control, the total sulfide concentration reached a high value of 445 mg/l S. Even with this high sulfide concentration, no toxicity resulted.

A comparison of the performance of this digester to the digester fed 1,200 mg/l S illustrates the role of solubility of the sulfides in determining the effect of sulfides on anaerobic treatment. The total sulfide concentrations in these two digesters were similar. However, gas production had completely terminated in the digester where the sulfides were almost all soluble, while the digester which contained this quantity of sulfides as the insoluble ferrous sulfide was almost unaffected. Thus, it appears that insoluble iron sulfides in concentrations up to at least 400 mg/l do not seriously affect anaerobic treatment, and that only soluble sulfide concentrations need to be considered in assessing the effects of sulfides on digester operation.

Sulfide Solubility

The quantity of soluble sulfides in the digester-supernatant liquor is related to several factors: (1) the total quantity entering and produced within the digester, (2) the quantity lost through precipitation by heavy metals and (3) the quantity which escapes with the gas.

The quantity of soluble sulfides which escapes with the gas is considerable. For example, the soluble sulfide concentration in the unit fed 800 mg/l S was only 1/4th of the feed concentration, or approximately 200 mg/l S. This large reduction in soluble sulfides is almost entirely due to the sulfide lost by the daily expulsion of gas. The quantity of sulfides lost in the gas is related to the relative quantity of gas produced each day, as well as the relationship between aqueous soluble sulfide and gaseous hydrogen sulfide as given in Equation 7.

The relationship between the quantity of soluble sulfides entering or formed within the digester and the quantity which is lost in the gas is as follows:

$$V_w S_w = V_g S_g + V_w S_e \qquad (8)$$

where, V_w = volume of waste entering or leaving digester per day,

V_g = volume of gas produced per day,

S_w = concentration in mg/l of soluble sulfides or soluble sulfide precursors in the raw waste.

S_g = sulfide concentration in mg/l in gas produced,

S_e = soluble sulfide concentration in mg/l in digester effluent.

The ratio of soluble sulfides in the digester effluent to that in the gas at equilibrium is rated to Equation 7 as follows:

$$\frac{S_e}{S_g} = \frac{[T.S.S.]}{[H_2S_g]} = \alpha \left(1 + \frac{K_1}{[H^+]}\right) = A \qquad (9)$$

Here, A is a constant for any given pH and temperature. Combining Equations 8 and 9 gives:

$$V_w S_w = V_g S_e / A + V_w S_e \qquad (10)$$

or,

$$\frac{S_e}{S_w} = \frac{1}{1 + V_g/AV_w} \qquad (11)$$

The relationships between pH and the ratio of total soluble sulfide concentration in the waste during treatment and hydrogen sulfide concentration in the gas calculated from Equation 9, for three different temperatures, are shown in Figure 8. Temperature can be seen to have only a small influence. Experimental ratios determined from measured sulfide values are also shown in this figure. The experimental values lie somewhat above the theoretical curves in all cases. Closer agreement would have been obtained if activity rather than molar concentration were used in Equation 9. In addition, removal of hydrogen sulfide from the gas due to absorption into the confining fluid in the gas collection tubes tended to give higher results than expected. It would also be expected that without continuous feed and complete mixing between the gases and supernatant liquor phase, complete equilibrium would not be obtained, causing a discrepancy between the theoretical and measured values. In spite of these differences, however, the experimental data adequately substantiates the developed relationship of Equation 9.

Equation 11 is shown graphically in Figure 9. Here, the influence of gas production and sulfide solubility (A) on the fraction of soluble sulfides remaining in solution can be seen. From Figure 8, it can also be seen that values of A varying from 4 to 8 could be expected for normal digester operation near a neutral pH. With these values, Figure 9 indicates that the fraction of soluble sulfide remaining in solution is inversely proportional to the volume of gas produced per unit volume of waste. Since more concentrated wastes will tend to produce more gas per unit volume, the fraction of sulfides remaining in solution for these wastes will tend to be lower. Thus, higher concentrations of sulfide precursors can be tolerated in more concentrated wastes as larger portions will be removed from solution by the greater quantities of gas produced.

For example, a 3 percent waste would have a ratio of gas production per unit volume of waste of about 20, and the fraction of soluble sulfides remaining in solution would be about 25 percent. For comparison, a 1 percent waste would have a ratio of about 7, and the fraction of soluble sulfides remaining would be about 45 percent. One other important point is that once the gas production began to decrease due to sulfide inhibition, less sulfides would be driven from solution, the sulfide concentration in solution would then rise higher, causing more inhibition. This cyclic toxic effect was observed in this study, and rapidly results in total cessation of gas production.

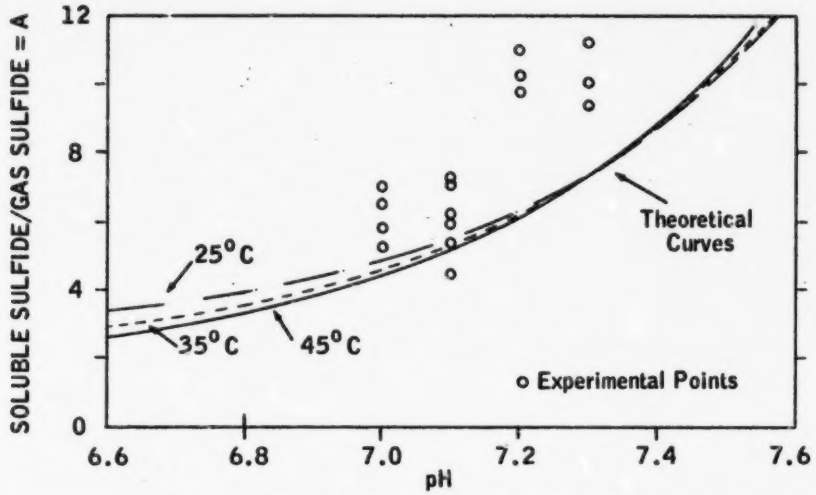


Figure 8 - Effect of pH on Ratio of Soluble Sulfide Concentration to Sulfide Concentration in Gas

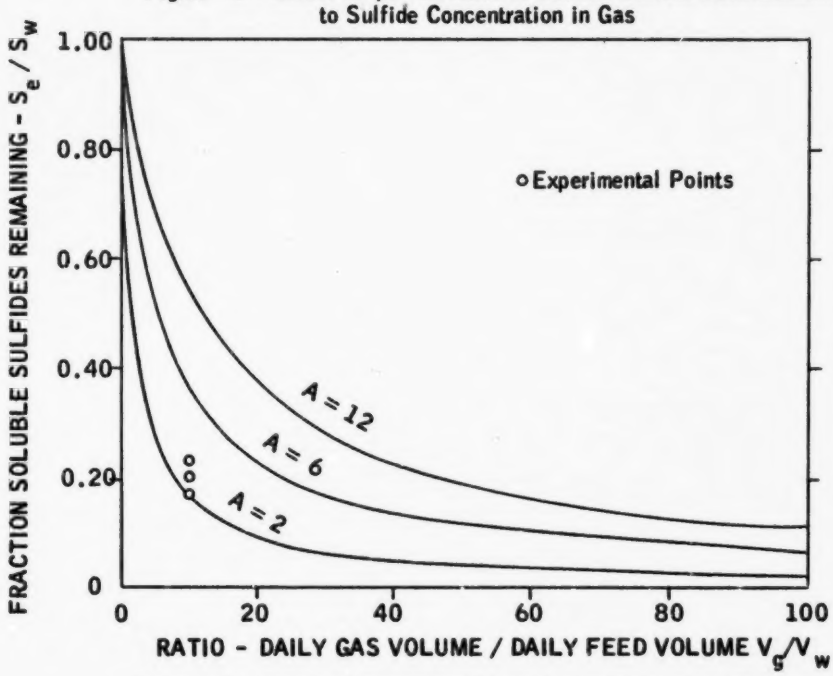


Figure 9 - Effect of Operational Variables on Fraction of Sulfides Remaining in Digester Effluent

Experimental points representing average values from this study are shown in Figure 9. These points are for operation at pH of 7.1 and 7.3, and the calculated A values varied from about 4.5 to 7. The points can be seen to be a little low, due mainly to the fact that a fair portion of the sulfides were removed from the gas by absorption into the gas retaining fluid. The theoretical values represented by the drawn curves would be more conservative and are what would be expected in field operation.

Precipitation of Toxic Sulfides

This study has shown that relatively high sulfur concentrations can be tolerated in a daily fed digester receiving a concentrated waste, since a good portion of the sulfides are removed along with the gas removed. One significant problem from removal of the sulfides with the gas is that the gas would be quite corrosive, and gas-handling facilities would have to be well protected. (For example, the successfully operated 800 mg/l S unit had about 20 mg/l of sulfides in the gas, representing 1.6 percent of the gas by volume, or approximately 880 grains per 100 cu.ft.) Another way to prevent a toxic sulfide concentration would be to precipitate the sulfides with iron as originally suggested by Rudolfs and Amberg[5]. This could be accomplished either externally by gas recirculation or internally by adding iron compounds to the waste. As shown here, concentrations of iron sulfide up to 400 mg/l S could be tolerated with only minor effects on the operation of the treatment process. Such an approach might be beneficial for more dilute wastes. An amount of iron salts such as ferric chloride equivalent to the waste sulfide concentration could be added to the digester. It might also be necessary to add sufficient base to the system to compensate for the decrease in alkalinity from ferric chloride additions.

The continuous addition of iron salts for sulfide control should give few operational problems. Present studies in this laboratory have demonstrated that the continual addition of at least 1,400 mg/l of iron, fed as ferric chloride, has a relatively minor effect on gas production and volatile acid production. This iron addition was in excess of that required to precipitate the sulfides present. Thus, excessive iron concentrations are not harmful. Use of iron to precipitate sulfides could therefore be used on a continuous basis to reduce sulfide toxicity, or else could be used on a slug basis to overcome the inhibitory effect of a sudden increase in sulfide concentration.

Summary and Conclusions

The effects of soluble and insoluble sulfides on anaerobic treatment have been investigated by the operation of a series of laboratory digesters receiving daily sulfide additions. A theoretical discussion of the chemical relationships governing the species of soluble sulfide and concentrations of sulfide in the aqueous and in the gas phases has been presented. Experimental results have been discussed with respect to toxic concentrations of soluble sulfides, and also with respect to agreement with the developed relationships. Possible methods for controlling or eliminating the sulfide toxicity have been discussed. The following conclusions may be drawn from this study:

1. Equilibrium concentrations of soluble sulfide up to 200 mg/l S exert no significant toxic effects on anaerobic treatment, with daily feed operation.
2. Concentrations of soluble sulfide higher than 200 mg/l S produce severe toxic effects and complete cessation of gas production.
3. Inhibitory concentrations of sulfides affect gas production first, while significant volatile acid accumulation takes place much slower, and only after gas production has been severely retarded.
4. Iron can be used to "inactivate" sulfides or reduce sulfide toxicity by precipitating sulfides from the biological environment.
5. Insoluble iron sulfide has no significant effect on anaerobic treatment up to a concentration of at least 400 mg/l of sulfide.
6. The concentration of sulfides in solution in the digester is related to the concentration of soluble sulfides and sulfide precursors entering with the waste, minus the quantity of sulfides expelled with the digester gas.
7. The quantity of sulfides lost with the daily gas is related to the solubility of hydrogen sulfide, the digester pH, and the relative daily gas production.

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